



## Screening of novel selected rare earths polychelates of 2,4-dihydroxy benzophenone resins as a catalyst for selected Beginili reactions

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### Publication History

Received: 09 June 2014

Accepted: 25 July 2014

Published: 1 August 2014

### Citation

Nileshkumar M Baria, Saiyogita Sharma, Patel Vasant M, Joshi JD. Screening of novel selected rare earths polychelates of 2,4-dihydroxy benzophenone resins as a catalyst for selected Beginili reactions. *Discovery*, 2014, 22(74), 86-101

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### General Note



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### ABSTRACT

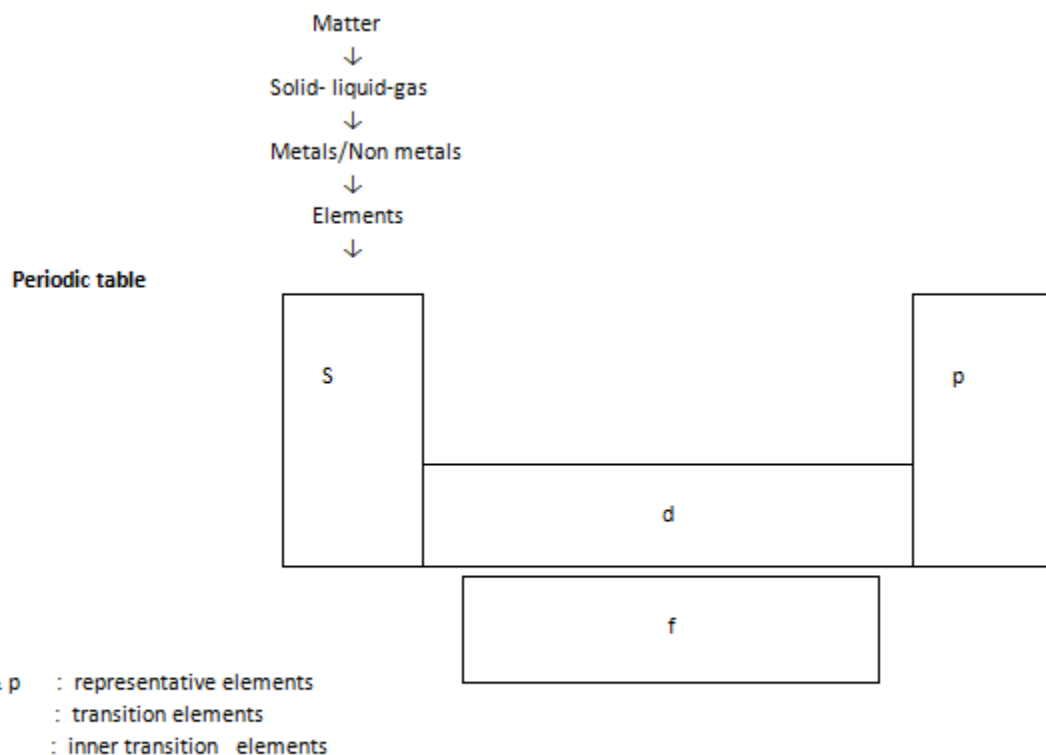
Synthesis of monomer 2,4-dihydroxy Benzophenone (DHBP) was carried out from resorcinol. The resins poly [(2,4- dihydroxy Benzophenone) ethylene, was synthesized using DHBP with ethane diol. Synthesised resin was used to prepare polychelates of La(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III) and Dy(III), Monomer, resin and polychelates were characterized using modern analytical methods. The application of polychelates was studied as a catalyst for various beginelli reactions.

**Keywords:** Monomer, Resin, Polychelates, Lanthanides, Catalyst.

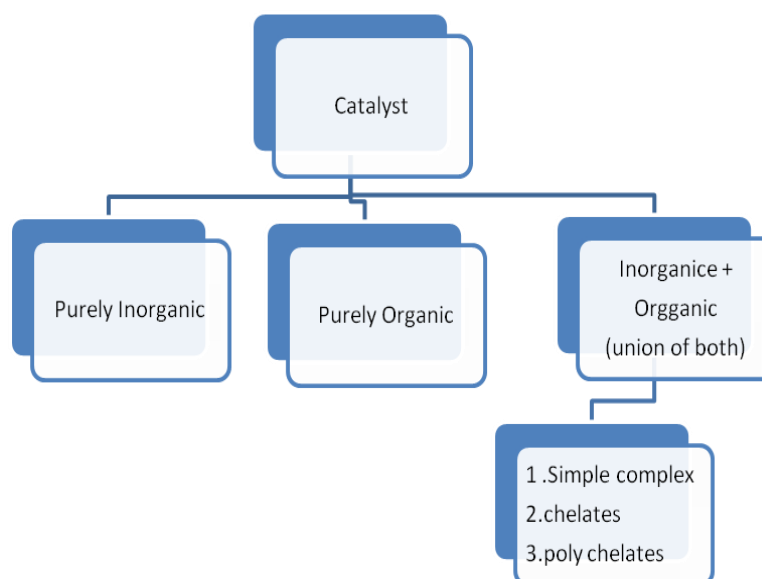
**Abbreviation:** 3,4-DHPM- 3,4 - dihydropyrimidin-2(1H)-ones; 2,4 - dihydroxy benzophenone; [DHBP-ED]<sub>n</sub>- poly[(2,4-dihydroxybenzophenone)ethylene]; DMSO- dimethyl sulphoxide; DMF- Dimethyl formamide, IR-infrared; MHz- megahertz; NMR- nuclear magnetic resonance; UV- ultraviolet; VPO- vapour pressure osmometry.

## 1. INTRODUCTION

The universe is composed of atmosphere, lithosphere and hydrosphere. The matter exists in solid, liquid, and gaseous forms. In chemistry classification of matter is given in a very systematic manner.



Amongst above all d and f elements and their compounds are very useful as a catalyst



The role of Ln (III)- phenol based polychelates as a catalyst (union of both i.e. inorganic + organic) for the synthesis of 3,4-dihydropyrimidines is very important and has got some additive and significant importance in the present catalyst and applied chemistry literature. Polymer-metal complexes have been of interest to many researchers during the past three decades in the light of their potential applications in diversified fields like organic synthesis (Thamizharasi and Balasubramanian, 1998), waste water treatment (Bessbousse et al. 2012), hydrometallurgy (Tasker et al. 2003), polymer drug grafting (Xue et al. 2011), recovery of trace metal ions (Koytepe and Seckin, 2009) and nuclear chemistry (Biederman and Holland, 1983). Metal uptake efficiency and reusability of the resin have been studied by Thammisetty et al., (2007). In addition, they have also used as modes for enzymes (Tang and Zhang, 2002; Martin-Matute, 2007). The metal polymer chelates obtained from nickel(II), cobalt(II), and titanium (IV), used as homogeneous catalysts, have been heterogenized by chelate formation with macro ligands act as efficient catalysts for polymerization of ethylene as well as butadiene (Ricci and Sommazzi, 2010).

The polymer supported catalysts preserve their homogenous character when examined on molecular basis, but are heterogeneous when considered on functional basis (Hadge and Sherrington, 1998; Backvall, 2004, Nair et al. 2003, De Vos and Sels, 2001). The simple work-up procedure, facile access to the active site by soluble reagents and the reusability of the catalyst are some of the significant advantages that these systems can offer (Sherrington, 1998). Polymer-supported materials are extensively used as oxidizing agents, reducing agents, photosensitizers or agriculturally and pharmacologically active reagents (Tonks and Williams, 1997). Recent studies have shown that transition metals in combination with various oxidizing agents convert a wide range of hydrocarbon of the corresponding oxidized products (Elemans and Bijterveld, 2000). These oxidations are moulded on certain enzymes that perform the oxidation of hydrocarbons in natural systems (Wang, 2006).

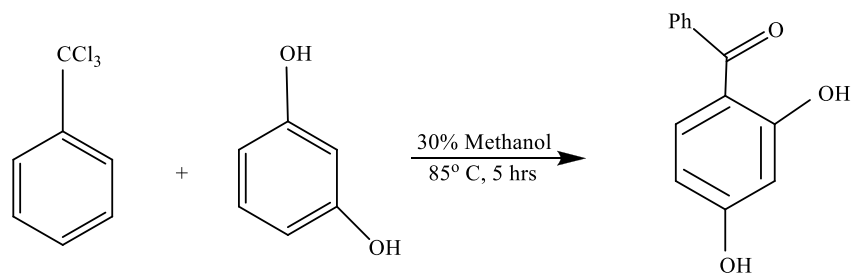
The applications of polymer-metal complexes in the field of catalysts have been highly investigated. Polymer-metal complexes are used as immobilized reagents useful for industrial purposes. Oxidation with molecular oxygen catalysed by transition metal complexes proved an attractive route for the preparation of synthetic intermediates and other oxygen containing organic substrates without the use of environmentally hazardous oxidants (Simandi, 1992). In the present work, we are reporting the simple synthetic protocol for the synthesis of polymer metal chelates, characterization and their uses as a catalyst.

## 2. MATERIALS AND METHODS

Benzotrichloride (Aldrich), resorcinol (S.D.Fine), ethane diol, 1,2 Propylene diol, 1,3 butane diol, 1,4 butane diol (Aldrich), polyphosphoric acid (PPA, Lancaster), Methanol, Ethanol, Acetone, Dimethyl Sulfoxide (DMSO) (Eliassi and Modarress, 2001), Hydrated metal acetates of Lanthanum, Praseodymium, Neodymium, Samarium, Terbium and Dysprosium (Merck). Double distilled water was used throughout the work.

### 2.1. Synthesis of 2,4-Dihydroxy Benzophenone (DHBP)

In a round bottom flask Benzotrichloride (19.55 gm, 0.1 mol) and resorcinol (11 gm, 0.1 mol) were placed. The aqueous methanol (30%, 140 mL) was added slowly with stirring to the reaction mixture. Then the resulting solution was refluxed at 85°C temp. for 5 hrs with constant stirring. Then the reaction mixture was allowed to cool and separated product at the bottom was collected by filtration. Then it was washed with hot water to remove unreacted resorcinol to give pale yellow needles of 2,4-dihydroxy benzophenone (DHBP) (Scheme 1).



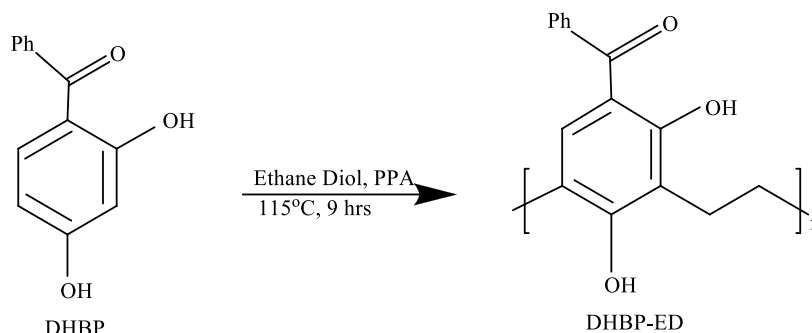
**Scheme 1**

Synthesis of 2,4-dihydroxy benzophenone

## 2.2. Synthesis of Resins

### Polycondensation of 2, 4 dihydroxy benzophenone with Ethane Diol

To a well stirred and ice –cooled mixture of 2,4 dihydroxy benzophenone (12.84 gm, 0.06 mol) and ethane diol (3.35mL, 0.06 mol), polyphosphoric acid (PPA) (20gm) was added slowly with stirring as a catalyst (Scheme 2). The reaction mixture was cooled and left at room temperature and condensed an oil bath at 115°C for 9 hrs. The reaction mixture was then cooled, poured on crushed ice and left overnight. A brown solid was separated acid and monomer. The synthesized resin was further purified by reprecipitation from dimethyl formamide (DMF) with water for three times and dried at 60°C temperature. The purified resin was reddish brown in color. D.P. > 265°C, Yield 42.80%.

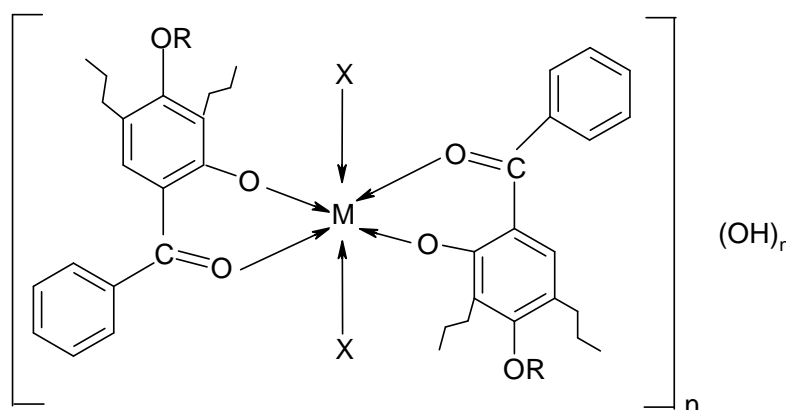


**Scheme 2**

Synthesis of DHBP-ED resin

## 2.3. Synthesis of Polychelates

The polymeric ligands DHBP-ED was used to synthesize polychelates of Ln(III) ions. Following general procedure has been established and used for several trials for the synthesis of polychelates from polymeric ligands. Hydrated acetates of lanthanum, Praseodymium, Neodymium, Samarium, Gadolinium, Terbium and Dysprosium were used for the synthesis of the polychelates. A dried polymeric ligand (0.01 mol) was dissolved in DMSO (50 mL). The metal acetate (0.005 mol) was also dissolved in DMSO (25 mL). The hot and clear solution of the metal acetate was added to the hot and clear solution of polymeric ligand with constant stirring. A dark colored product precipitated out immediately. The suspension was digested on a water bath for two hours and then filtered. The solid was washed with cold DMSO to remove unreacted metal acetate. Finally, the polychelate formed was washed with acetone and dried at 60°C for 24 hrs. The proposed geometry of the polychelate is given in scheme 3.



**Scheme 3**

proposed geometry of polychelates

M=La<sup>III</sup>, Pr<sup>III</sup>, Nd<sup>III</sup>, Sm<sup>III</sup>, Gd<sup>III</sup>, Tb<sup>III</sup>, Dy<sup>III</sup>

X=H<sub>2</sub>O

R=H

### 3. RESULTS AND DISCUSSION

Analytical data (Table 1) and other data present and discussed in the respective sections.

#### 3.1. FTIR spectra

FTIR Spectra of resin and all the synthesized polychelates are shown as figures 1-8.

#### 3.2. $^1\text{H}$ NMR Spectrum of DHBP-ED

The NMR spectrum of resin is shown as in figure 9.

**$^1\text{H}$  NMR (DMSO –  $d_6$ ):**  $\delta$  = 12.02 (s, phenolic OH, ortho to (Ar-Co)), 3.92 (q, 2H –Oet, para to (Ar-CO)), 3.35 (t, 2H, bridge), 3.17 (t, 2H, bridge), 7.23 – 7.66 (6H, Ar-H).

#### 3.3. Vapor pressure Osmometry (VPO)

An average molecular weight of the resin was determined using the technique and experimental process carried out same as earlier (Bonner and Dimbatt, 1958). The details of concentration, bridge output SD, Slope and ( $M_n$ ) calculation of the resins DHBP-ED, presented in table 2.

#### 3.4. Visible Spectra of Resins

The UV spectra of DHBP (Brian Milligan, Leo A., 1983) and its polymeric resins (DHBP-ED, DHBP-1,2 PD, DHBP-1,3 BD and DHBP-1,4 BD) shows bands at 289 and 390 nm due to  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  transition (Alsheri SM, Monshim AS, 2000). By proper selection of copolymer, useful UV-absorbing polymers with varying amount of UV-absorbing groups (DHBP) can be synthesized. DHBP has intermediate thermal properties and hence can remain in a blend resins during various applications and can also protect the resins from UV light.

#### 3.5. UV Visible Spectra of Polychelates

The data indicates the energy of  $f-f$  transitions in polychelates is slightly reduced compared to the corresponding aquo ions either because of the slight covalent interaction of the “4  $f$ ” orbitals with vacant ligand orbitals leading to some delocalization with consequent reduction in interelectronic repulsion (Kriza A, Reisa A, 2000) or by increased nuclear shielding of the orbitals due to slight covalent ligand-metal electron drift compared to the aquo ions of the lanthanides. The  $f-f$  transition bands of the polychelates show weak perturbation and increased intensity due to complex formation, presumably due to the nephelauxetic effect (Xu and Quan Li, 1996). The electronic spectra of all the polychelates exhibit the addition of two spectral bands in the resin 289-295 and 390-420 nm. The first band occurs in the spectra of polymeric ligand (resin). The spectra are showing similar behavior as reported earlier (Narang and Rao, 2000).

#### 3.6. Catalytic Study

##### Synthesis of substituted 3,4-dihydropyrimidine-2(1H)-ones

All substituted 3,4-dihydropyrimidine-2(1H) - ones were synthesized by following method. In a typical experimental reaction a solution of 1,3 diketone (0.1 mol) , aromatic aldehyde (0.1 mol) and urea (0.1 mol) in ethanol (40 ml) was refluxed at boiling temperature in presence of metal polychelate as a catalyst (1 gm), to give 3,4-dihydropyrimidine-2(1H) - ones as shown in Scheme 4. Progress of reaction was monitored by TLC. After completion of reaction, reaction mixture was then allowed to cool; crude product obtained was separated by filtration. The crude product was then dissolved in ethanol and filtered to remove insoluble catalyst and recrystallized. The separated catalyst can be reused by giving simple water treatment and after drying.

The mechanism of the Biginelli reaction may proceed through the imine intermediate formed from the aldehydes and urea, stabilized by polychelate (metal ion) followed by the addition of the  $\beta$ -ketoesterenolate and cyclodehydration to afford the 3,4-dihydropyrimidine-2(1H)-one (Scheme 4). So, the proposed mechanism similar to that of (Kappe, 1997) for polychelate promoted Biginelli reaction and results are presented in table 3-6.

### 4. CONCLUSION

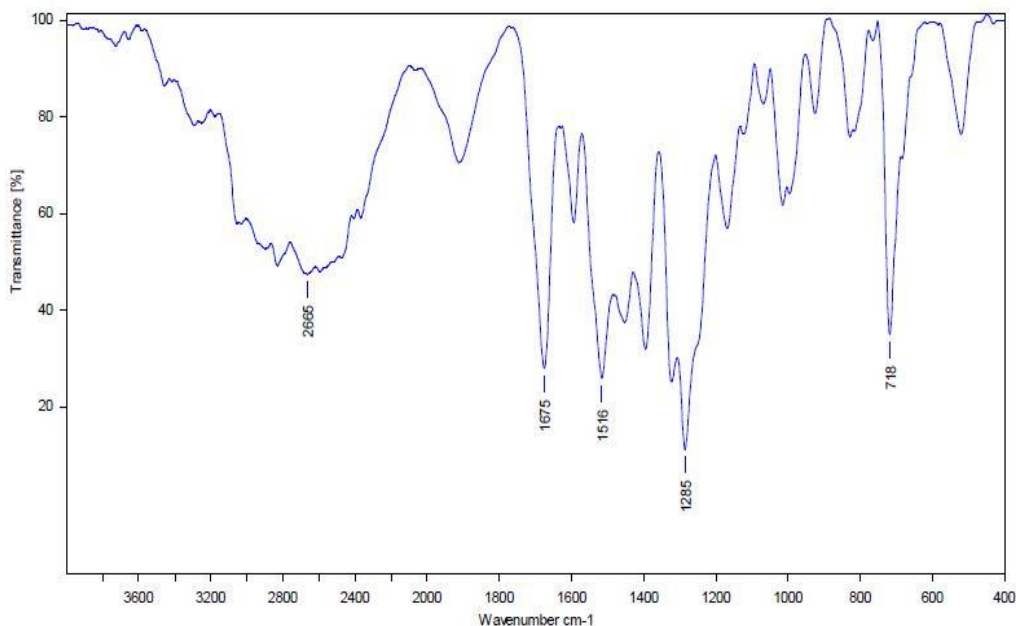
It is found that 2,4- dihydroxy benzophenone –Ethane diol resin- Ln(III) polychelates acts as an efficient, effective, time saving, kinetically fast and good yield giving quality product in studied Biginelli organic reactions.

**Table 1**

Analytical data of the DHBP-ED resin and its Polychelates

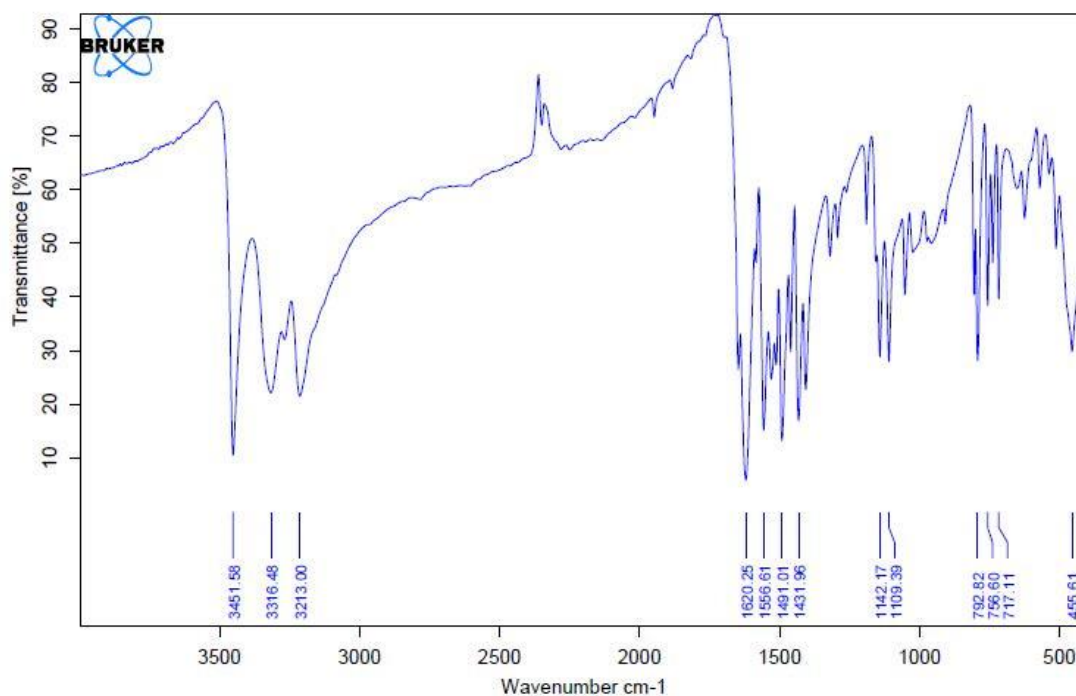
Compound	Formula weight of Repeating unit	% Found (Calculated)			$\mu_{\text{eff}}$ (B.M)
		M	C	H	
(DHBP-ED) <sub>n</sub> [C <sub>15</sub> H <sub>12</sub> O <sub>3</sub> ] <sub>n</sub>	240	---	75.00 (74.98)	5.00 (5.03)	---
{[La(DHBP-ED) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].OH} <sub>n</sub> [C <sub>30</sub> H <sub>27</sub> O <sub>9</sub> La] <sub>n</sub>	670	20.90 (20.71)	53.91 (53.74)	4.02 (4.05)	Diamagnetic
{[Pr(DHBP-ED) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].OH} <sub>n</sub> [C <sub>30</sub> H <sub>27</sub> O <sub>9</sub> Pr] <sub>n</sub>	672	21.00 (20.95)	53.51 (53.58)	4.03 (4.04)	3.66
{[Nd(DHBP-ED) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].OH} <sub>n</sub> [C <sub>30</sub> H <sub>27</sub> O <sub>9</sub> Nd] <sub>n</sub>	675	21.22 (21.34)	53.41 (53.32)	4.00 (4.02)	3.63
{[Sm(DHBP-ED) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].OH} <sub>n</sub> [C <sub>30</sub> H <sub>27</sub> O <sub>9</sub> Sm] <sub>n</sub>	681	22.03 (22.05)	52.93 (52.84)	3.95 (3.99)	1.72
{[Gd(DHBP-ED) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].OH} <sub>n</sub> [C <sub>30</sub> H <sub>27</sub> O <sub>9</sub> Gd] <sub>n</sub>	682	22.03 (22.05)	52.94 (52.84)	3.96 (3.99)	7.88
{[Tb(DHBP-ED) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].OH} <sub>n</sub> [C <sub>30</sub> H <sub>27</sub> O <sub>9</sub> Tb] <sub>n</sub>	690	23.10 (23.01)	52.30 (52.18)	3.90 (3.94)	9.46
{[Dy(DHBP-ED) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].OH} <sub>n</sub> [C <sub>30</sub> H <sub>27</sub> O <sub>9</sub> Dy] <sub>n</sub>	694	23.35 (23.41)	52.00 (51.91)	3.95 (3.92)	10.63

DHBP-ED = poly [(2,4-dihydroxybenzophenone)ethylene]

**Figure 1**

FTIR Spectrum of DHBP-1,2-ethane diol resin

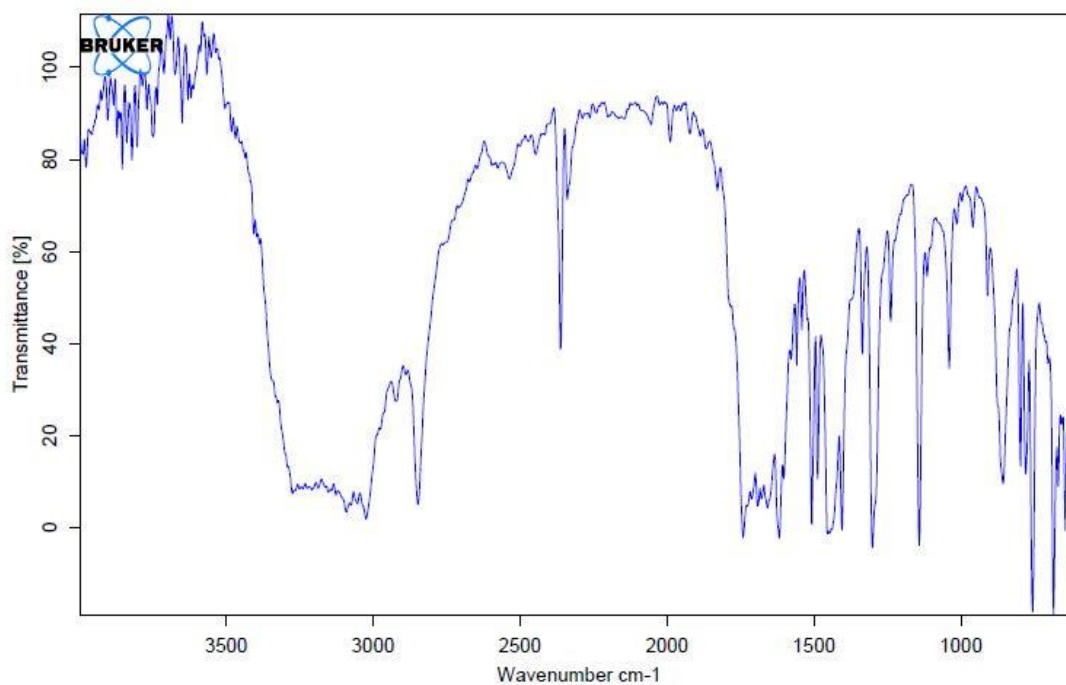
IR(KBr): 3200-3400 (-OH stretching), 2950-2980 (-CH<sub>2</sub> Stretching), 2735 (Intra mol. H-), 1635±10 (>C=O), 1590, 1560, 1525, 1495, (-C=C-), 1345 (-OH), 1280±10 (Ar-O-R), 995, 860 ± 10, 700 (Ph ring) cm<sup>-1</sup>.



**Figure 2**

FTIR Spectrum of  $[\text{La}(\text{DHBP-ED})_2(\text{H}_2\text{O})_2]\cdot\text{OH}_n$

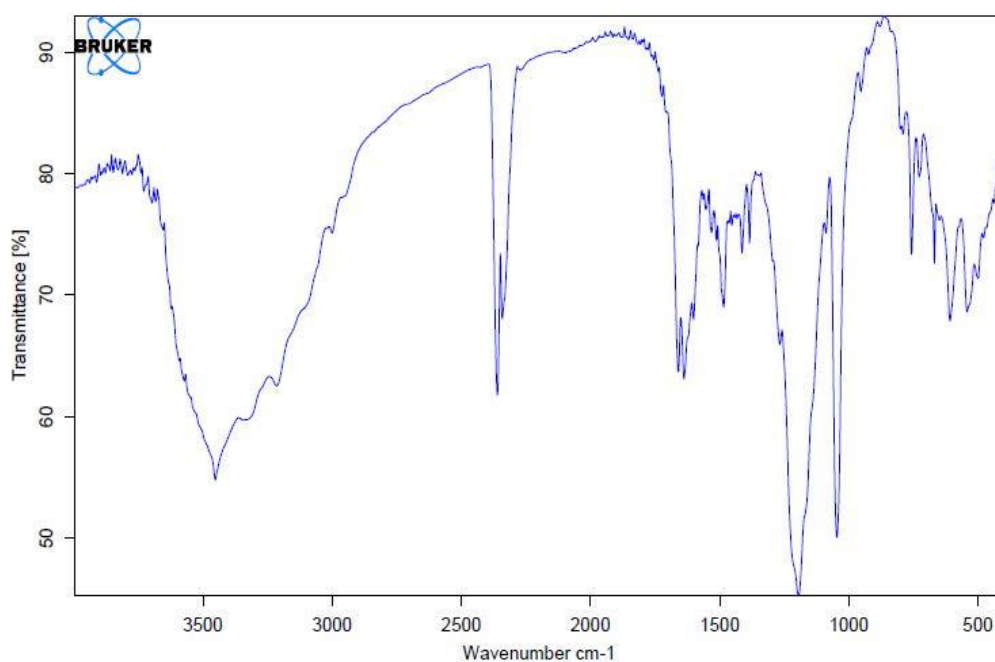
**IR(KBr):** 3100-3600 (-OH Stretching), 2950-2880 (-CH<sub>2</sub> stretching), 1620 ± 20 (>C=O), 1600-1540 (δ HOH), 1440-1600 (-C=C- aromatic), 1350-1340 (-OH), 1260 ± 15 (Ar-O-R), 960-1000, 700 ± 10 (Ph ring), 670-650, 565, 459-480 (M-O bond) cm<sup>-1</sup>.



**Figure 3**

FTIR Spectrum of  $[\text{Pr}(\text{DHBP-ED})_2(\text{H}_2\text{O})_2]\cdot\text{OH}_n$

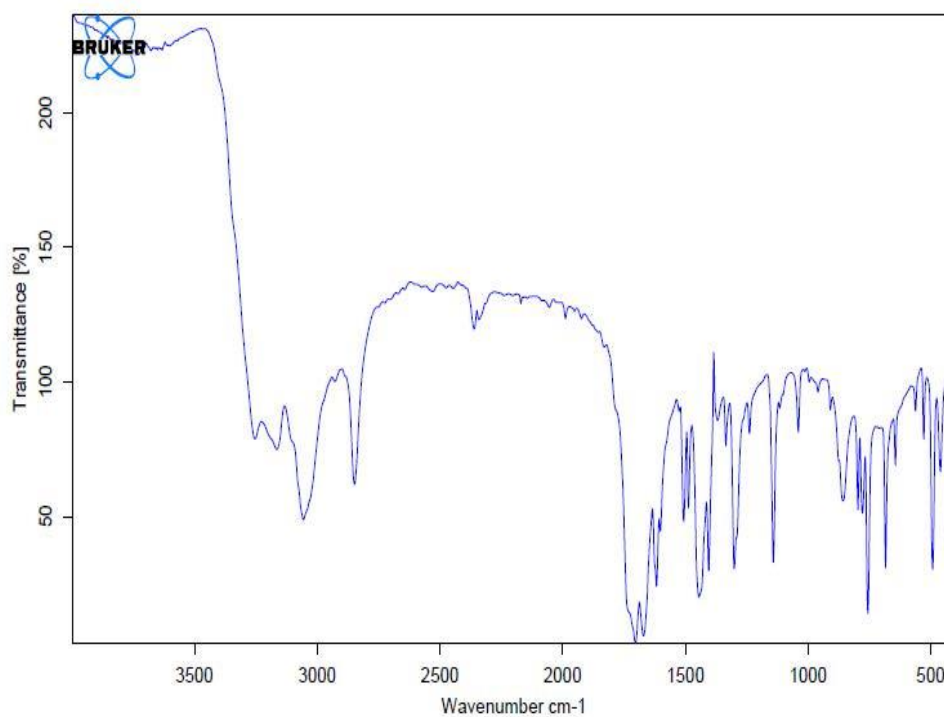
**IR(KBr):** 3100-3600 (-OH Stretching), 2950-2880 (-CH<sub>2</sub> stretching), 1620 ± 20 (>C=O), 1600-1540 (δ HOH), 1440-1600 (-C=C- aromatic), 1350-1340 (-OH), 1260 ± 15 (Ar-O-R), 960-1000, 700 ± 10 (Ph ring), 670-650, 565, 459-480 (M-O bond) cm<sup>-1</sup>.



**Figure 4**

FTIR Spectrum of  $[\text{Nd}(\text{DHBP-ED})_2(\text{H}_2\text{O})_2]\cdot\text{OH}_n$

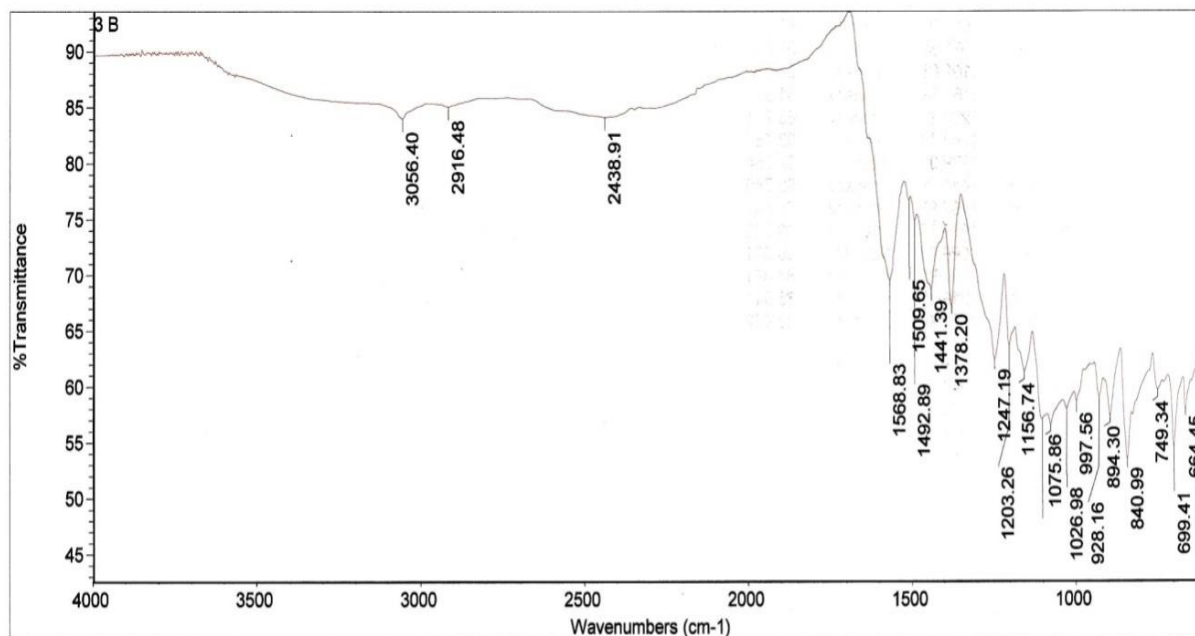
**IR(KBr):** 3100-3600 (-OH Stretching), 2950-2880 (-CH<sub>2</sub> stretching),  $1620 \pm 20$  (>C=O), 1600-1540 ( $\delta$  HOH), 1440-1600 (-C=C- aromatic), 1350-1340 (-OH),  $1260 \pm 15$  (Ar-O-R), 960-1000,  $700 \pm 10$  (Ph ring), 670-650, 565, 459-480 (M-O bond) cm<sup>-1</sup>.



**Figure 5**

FTIR Spectrum of  $[\text{Sm}(\text{DHBP-ED})_2(\text{H}_2\text{O})_2]\cdot\text{OH}_n$

**IR(KBr):** 3100-3600 (-OH Stretching), 2950-2880 (-CH<sub>2</sub> stretching),  $1620 \pm 20$  (>C=O), 1600-1540 ( $\delta$  HOH), 1440-1600 (-C=C- aromatic), 1350-1340 (-OH),  $1260 \pm 15$  (Ar-O-R), 960-1000,  $700 \pm 10$  (Ph ring), 670-650, 565, 459-480 (M-O bond) cm<sup>-1</sup>.



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FIND PEAKS:

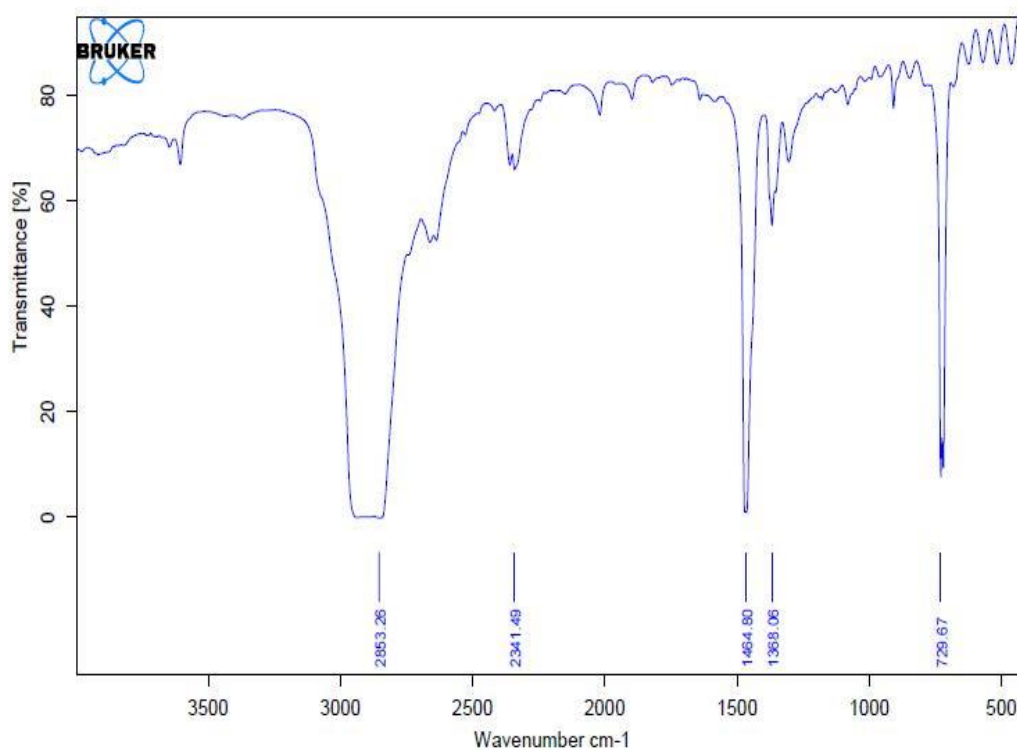
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 Region: 4000.00 600.00  
 Absolute threshold: 87.239  
 Sensitivity: 86  
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Position:	699.41	Intensity:	54.590
Position:	749.34	Intensity:	59.660
Position:	840.99	Intensity:	53.491
Position:	894.30	Intensity:	57.387
Position:	928.16	Intensity:	59.082
Position:	997.56	Intensity:	58.711
Position:	1026.98	Intensity:	57.983
Position:	1075.86	Intensity:	56.514
Position:	1101.85	Intensity:	57.019
Position:	1156.74	Intensity:	61.374
Position:	1203.26	Intensity:	63.721
Position:	1247.19	Intensity:	62.457
Position:	1378.20	Intensity:	67.254
Position:	1441.39	Intensity:	68.740
Position:	1492.89	Intensity:	74.899
Position:	1509.65	Intensity:	76.726
Position:	1568.83	Intensity:	69.571
Position:	2438.91	Intensity:	84.091
Position:	2916.48	Intensity:	85.041
Position:	3056.40	Intensity:	83.972

**Figure 6**

FTIR Spectrum of  $[[\text{Gd}(\text{DHBP-ED})_2(\text{H}_2\text{O})_2]\cdot\text{OH}]_n$

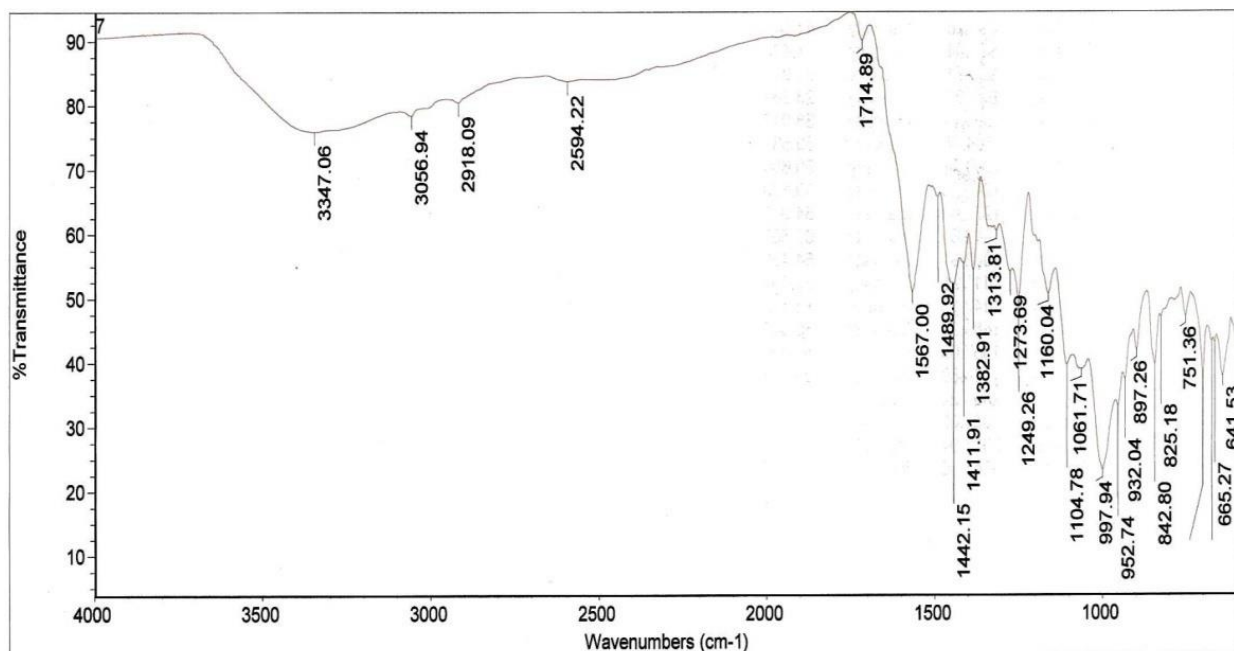
**IR(KBr):** 3100-3600 (-OH Stretching), 2950-2880 (-CH<sub>2</sub> stretching), 1620 ± 20 (>C=O), 1600-1540 (δ HOH), 1440-1600 (-C=C- aromatic), 1350-1340 (-OH), 1260 ± 15 (Ar-O-R), 960-1000, 700 ± 10 (Ph ring), 670-650 (M-O bond) cm<sup>-1</sup>.



**Figure 7**

FTIR Spectrum of  $[\text{Tb}(\text{DHBP-ED})_2(\text{H}_2\text{O})_2]\cdot\text{OH}_n$

**IR(KBr):** 3100-3600 (-OH Stretching), 2950-2880 (-CH<sub>2</sub> stretching), 1620 ± 20 (>C=O), 1600-1540 (δ HOH), 1440-1600 (-C=C-aromatic), 1350-1340 (-OH), 1260 ± 15 (Ar-O-R), 960-1000, 700 ± 10 (Ph ring), 670-650, 565, 459-480 (M-O bond) cm<sup>-1</sup>.



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FIND PEAKS:

Spectrum: 7  
 Region: 4000.00 600.00  
 Absolute threshold: 93.309  
 Sensitivity: 92  
 Peak list:

Position:	641.53	Intensity:	37.781
Position:	665.27	Intensity:	43.025
Position:	673.69	Intensity:	43.233
Position:	700.17	Intensity:	38.359
Position:	751.36	Intensity:	47.111
Position:	825.18	Intensity:	47.031
Position:	842.80	Intensity:	39.748

Position:	897.26	Intensity:	41.941
Position:	932.04	Intensity:	37.403
Position:	952.74	Intensity:	33.219
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Position:	1104.78	Intensity:	39.581
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Position:	1382.91	Intensity:	54.450
Position:	1411.91	Intensity:	55.407
Position:	1442.15	Intensity:	52.118
Position:	1489.92	Intensity:	65.819
Position:	1567.00	Intensity:	51.003
Position:	1714.89	Intensity:	90.071
Position:	2594.22	Intensity:	83.722
Position:	2918.09	Intensity:	80.416
Position:	3056.94	Intensity:	78.372
Position:	3347.06	Intensity:	75.900

**Figure 8**

FTIR Spectrum of  $[\text{Dy}(\text{DHBP-ED})_2(\text{H}_2\text{O})_2]\cdot\text{OH}_n$

**IR(KBr):** 3100-3600 (-OH Stretching), 2950-2880 (-CH<sub>2</sub> stretching), 1620 ± 20 (>C=O), 1600-1540 (δ HOH), 1440-1600 (-C=C- aromatic), 1350-1340 (-OH), 1260 ± 15 (Ar-O-R), 960-1000, 700 ± 10 (Ph ring), 670-650 (M-O bond) cm<sup>-1</sup>.

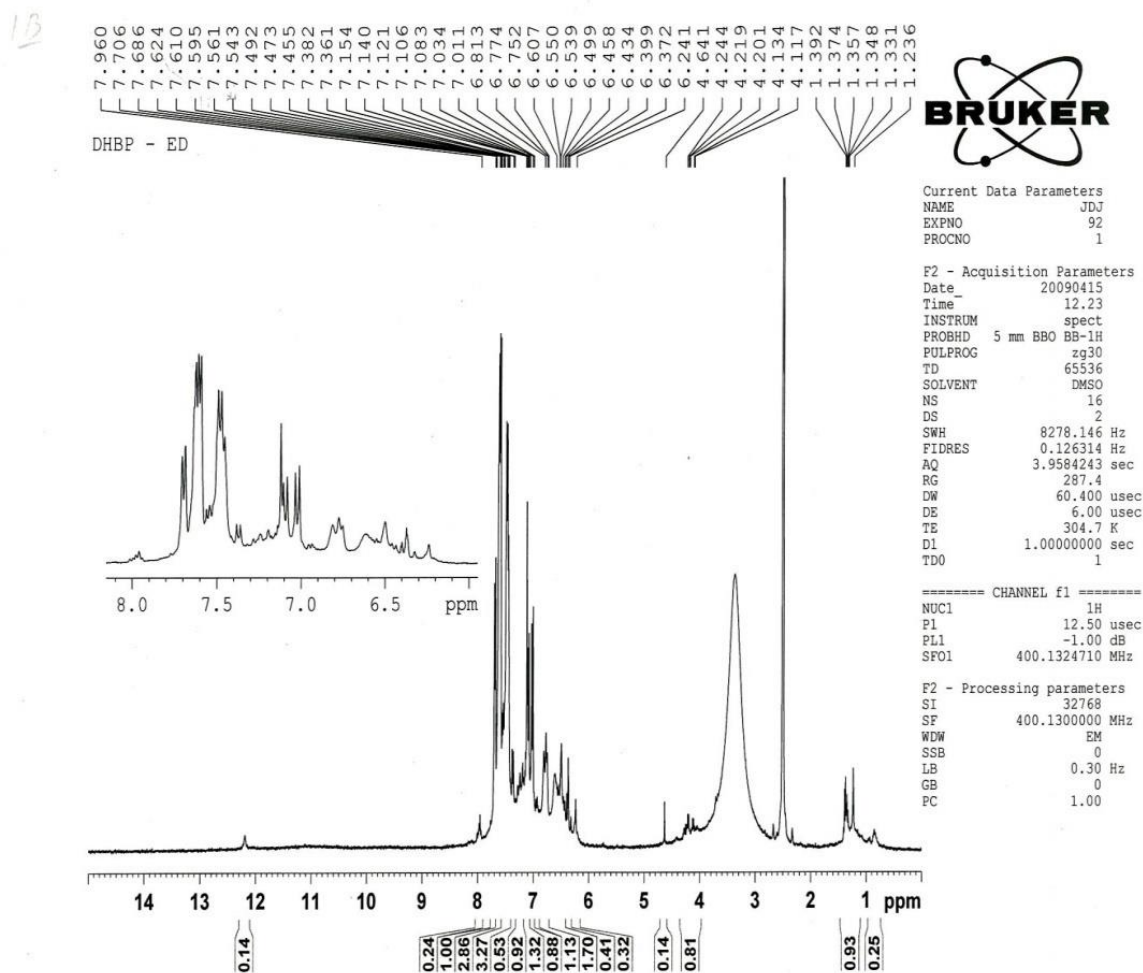


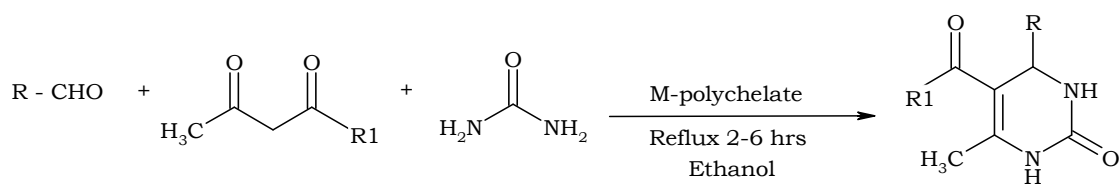
Figure 9

<sup>1</sup>H NMR Spectrum of DHBP-ED Resins

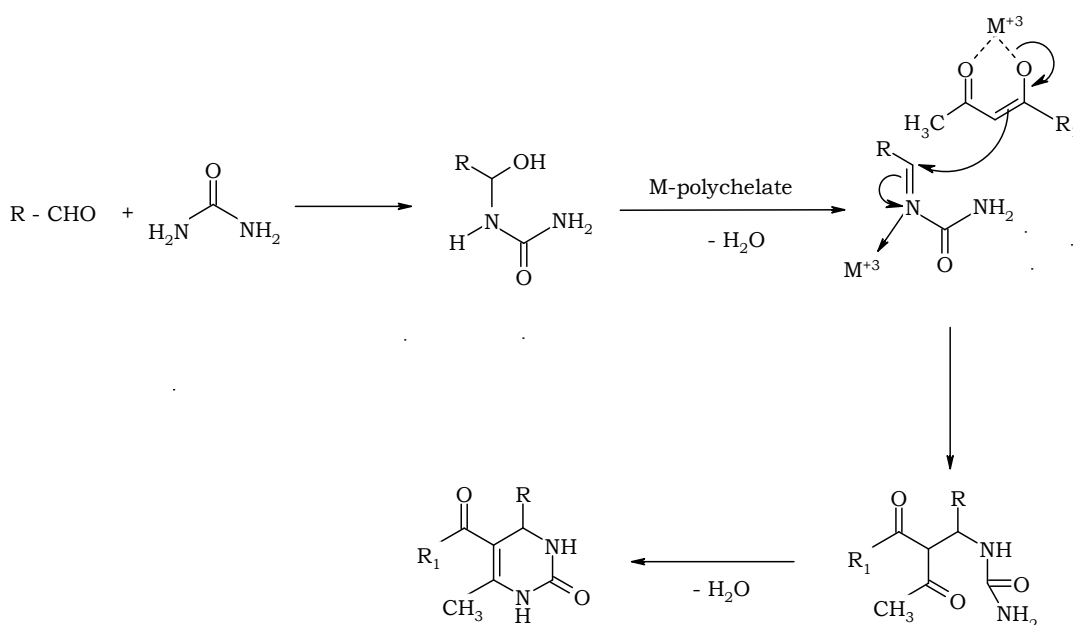
Table 2

Molecular Weight Determination of Resins by VPO Method

Resin	Conc. Gm.mol <sup>-1</sup>	S.D. Millivolts	Slope of Plot	$\overline{M}_n = K/\text{slope g.mol}^{-1}$
DHBP-ED	2.21	22.00	9.39	1124
	4.48	43.00		
	6.63	65.00		
	8.84	85.00		
	2.21	21.00		



### Mechanism



R = -C<sub>6</sub>H<sub>5</sub>, 4-OH-C<sub>6</sub>H<sub>4</sub>, 4-OMe-C<sub>6</sub>H<sub>4</sub>, 4-OH-3-OMe-C<sub>6</sub>H<sub>3</sub>, 4-Cl-C<sub>6</sub>H<sub>4</sub>

R<sub>1</sub> = -OC<sub>2</sub>H<sub>5</sub>, -CH<sub>3</sub>

M = La(III), Pr(III), Nd(III) and Sm(III)

### Scheme 4

Synthesis of 3,4-dihydropyrimidine-2(1H)-ones

**Table 3**

{[La(DHBP-ED)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>].OH}<sub>n</sub> Catalyzed Synthesis of Substituted 3,4-Dihydropyrimidine-2(1H)-Ones

Sr. No.	R	R <sup>1</sup>	Time (hrs)	Yield (%)	m.p. °C	
					Found	Reported
1	C <sub>6</sub> H <sub>5</sub>	OEt	2	91	201	202-204
2	4-OH-C <sub>6</sub> H <sub>5</sub>	OEt	4	89	198	199-200
3	4-OMe-C <sub>6</sub> H <sub>5</sub>	OEt	2	91	200	200-201
4	4-OH-3-OMe-C <sub>6</sub> H <sub>5</sub>	OEt	6	91	209	208-211
5	4-Cl-C <sub>6</sub> H <sub>4</sub>	OEt	5	88	214	213-214
6	C <sub>6</sub> H <sub>5</sub>	Me	2	91	232	234-235
7	4-OH-C <sub>6</sub> H <sub>5</sub>	Me	4	89	208	210-211
8	4-OMe-C <sub>6</sub> H <sub>5</sub>	Me	2	88	180	178-180

9	4-OH-3-OMe-C <sub>6</sub> H <sub>5</sub>	Me	6	91	245	246-248
10	4-Cl-C <sub>6</sub> H <sub>4</sub>	Me	5	86	214	215-216

**Table 4**

{[Pr(DHBP-ED)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>].OH}<sub>n</sub> Catalyzed Synthesis of Substituted 3,4-Dihydropyrimidine-2(1H)-Ones

Sr. No.	R	R <sup>1</sup>	Time (hrs)	Yield (%)	m.p. °C	
					Found	Reported
1	C <sub>6</sub> H <sub>5</sub>	OEt	2	90	201	202-204
2	4-OH-C <sub>6</sub> H <sub>5</sub>	OEt	4	90	198	199-200
3	4-OMe-C <sub>6</sub> H <sub>5</sub>	OEt	2	89	200	200-201
4	4-OH-3-OMe-C <sub>6</sub> H <sub>5</sub>	OEt	6	92	209	208-211
5	4-Cl-C <sub>6</sub> H <sub>4</sub>	OEt	5	90	214	213-214
6	C <sub>6</sub> H <sub>5</sub>	Me	2	91	232	234-235
7	4-OH-C <sub>6</sub> H <sub>5</sub>	Me	4	89	208	210-211
8	4-OMe-C <sub>6</sub> H <sub>5</sub>	Me	2	90	180	178-180
9	4-OH-3-OMe-C <sub>6</sub> H <sub>5</sub>	Me	6	92	245	246-248
10	4-Cl-C <sub>6</sub> H <sub>4</sub>	Me	5	90	214	215-216

**Table 5**

{[Nd(DHBP-ED)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>].OH}<sub>n</sub> Catalyzed Synthesis of Substituted 3,4-Dihydropyrimidine-2(1H)-Ones

Sr. No.	R	R <sup>1</sup>	Time (hrs)	Yield (%)	m.p. °C	
					Found	Reported
1	C <sub>6</sub> H <sub>5</sub>	OEt	2	91	201	202-204
2	4-OH-C <sub>6</sub> H <sub>5</sub>	OEt	4	90	198	199-200
3	4-OMe-C <sub>6</sub> H <sub>5</sub>	OEt	2	90	200	200-201
4	4-OH-3-OMe-C <sub>6</sub> H <sub>5</sub>	OEt	6	92	209	208-211
5	4-Cl-C <sub>6</sub> H <sub>4</sub>	OEt	5	90	214	213-214
6	C <sub>6</sub> H <sub>5</sub>	Me	2	91	232	234-235
7	4-OH-C <sub>6</sub> H <sub>5</sub>	Me	4	90	208	210-211
8	4-OMe-C <sub>6</sub> H <sub>5</sub>	Me	2	91	180	178-180
9	4-OH-3-OMe-C <sub>6</sub> H <sub>5</sub>	Me	6	93	245	246-248
10	4-Cl-C <sub>6</sub> H <sub>4</sub>	Me	5	89	214	215-216

**Table 6**

{[Sm(DHBP-ED)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>].OH}<sub>n</sub> Catalyzed Synthesis of Substituted 3,4-Dihydropyrimidine-2(1H)-Ones

Sr. No.	R	R <sup>1</sup>	Time (hrs)	Yield(%)	m.p. °C	
					Found	Reported
1	C <sub>6</sub> H <sub>5</sub>	OEt	2	91	201	202-204
2	4-OH-C <sub>6</sub> H <sub>5</sub>	OEt	4	89	198	199-200
3	4-OMe-C <sub>6</sub> H <sub>5</sub>	OEt	2	91	200	200-201
4	4-OH-3-OMe-C <sub>6</sub> H <sub>5</sub>	OEt	6	93	209	208-211
5	4-Cl-C <sub>6</sub> H <sub>4</sub>	OEt	5	90	214	213-214

6	C <sub>6</sub> H <sub>5</sub>	Me	2	89	232	234-235
7	4-OH-C <sub>6</sub> H <sub>5</sub>	Me	4	91	208	210-211
8	4-OMe-C <sub>6</sub> H <sub>5</sub>	Me	2	90	180	178-180
9	4-OH-3-OMe-C <sub>6</sub> H <sub>5</sub>	Me	6	91	245	246-248
10	4-Cl-C <sub>6</sub> H <sub>4</sub>	Me	5	92	214	215-216

## SUMMARY OF RESEARCH

1. The La(III) polychelates of phenolic resin were developed as potential catalyst for the efficient one-pot synthesis of 3,4-dihydropyrimidin-2(1H)ones. The reactivity of the reactants were evaluated using different aldehyde derivatives and two substituted 1,3-diketones.
2. In most of the cases, the 3,4-dihydropyrimidin-2(1H)-ones were synthesized with a short reaction time of about 2-6 h and 87-92 % yields, using the synthesized polychelate catalysts. Furthermore, they could be effectively and easily regenerated by simple treatment of water.

## FUTURE ISSUES

The catalytic effects of the catalysts may be evaluated for the synthesis of a variety of a substrates 3,4-Dihydropyrimidin-2(1H)ones(DHMP) and their analogues. In addition, due to high clinical relevance of some of the DHMP and their sulfur analogues, studies may be carried out to improve the catalytic activities and the existing synthesis routes for the preparation of pharmaceutical products based on DHMP.

## DISCLOSURE STATEMENT

There is no financial support for this research work from any funding agency.

## ACKNOWLEDGEMENT

Authors are thankful to the Institution Head for providing necessary facilities.

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